

Spin and orbital states in  $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$  studied by electronic structure calculationsHua Wu<sup>1</sup> and T. Burnus<sup>2</sup><sup>1</sup>*II. Physikalisches Institut, Universität zu Köln, Zùlpicher Str. 77, 50937 Köln, Germany*<sup>2</sup>*Institut für Festkörperforschung, Forschungszentrum Jùlich, 52425 Jùlich, Germany*

(Received 24 July 2009; published 26 August 2009)

Electronic structure of the layered perovskite  $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$  with a checkerboard  $\text{Co}^{2+}/\text{Co}^{3+}$  charge order is studied, using the local-spin-density approximation plus Hubbard  $U$  calculations including also the spin-orbit coupling and multiplet effect. Our results show that the  $\text{Co}^{2+}$  ion is in a high spin state ( $\text{HS}, t_{2g}^5 e_g^2$ ) and  $\text{Co}^{3+}$  low spin state ( $\text{LS}, t_{2g}^6$ ). Due to a small  $\text{Co}^{2+}$   $t_{2g}$  crystal field splitting, the spin-orbit interaction produces an orbital moment of  $0.26\mu_B$  and accounts for the observed easy in-plane magnetism. Moreover, we find that the  $\text{Co}^{3+}$  intermediate spin state ( $\text{IS}, t_{2g}^5 e_g^1$ ) has a multiplet splitting of several tenths of eV and the lowest-lying one is still higher than the LS ground state by 120 meV, and that the  $\text{Co}^{3+}$  HS state ( $t_{2g}^4 e_g^2$ ) is more unstable by 310 meV. Either the IS or HS  $\text{Co}^{3+}$  ions would give rise to a wrong magnetic order and anisotropy.

DOI: [10.1103/PhysRevB.80.081105](https://doi.org/10.1103/PhysRevB.80.081105)

PACS number(s): 71.20.-b, 71.27.+a, 71.70.-d, 75.30.-m

Cobaltates comprise a group of interesting materials which display spectacular properties such as superconductivity,<sup>1</sup> giant magnetoresistance,<sup>2</sup> and large thermoelectric power.<sup>3</sup> One aspect in the physics of cobaltates, which distinguishes them from other transition metal oxides, is the spin state issue, particularly for the  $\text{Co}^{3+}$  ions. It can be a low spin (LS), a high spin (HS), or even an intermediate spin (IS) state, depending on a subtle interplay among crystal field, Hund exchange, multiplet effects, and spin-orbit coupling (SOC).<sup>4-17</sup> One prototype material is the perovskite  $\text{LaCoO}_3$ , and its temperature-dependent spin state transition has been extensively studied but a consensus has not yet been reached so far: the magnetic excitations at about 100 and 500 K in  $\text{LaCoO}_3$  have been ascribed to either an  $\text{LS} \rightarrow \text{HS}$  transition,<sup>4-9</sup> an  $\text{LS} \rightarrow \text{IS}$  transition,<sup>10-13</sup> or  $\text{LS} \rightarrow (\text{LS} + \text{HS}) \rightarrow \text{IS}$  transitions.<sup>14-17</sup>

Recently, the single layered perovskite  $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$  received considerable attention for its extremely insulating behavior, peculiar magnetic correlations, and doping-dependent charge/spin superstructures, and its spin state issue becomes a vital topic.<sup>18-26</sup> The parent compound  $\text{La}_2\text{CoO}_4$  has a normal HS  $\text{Co}^{2+}$  and is an antiferromagnetic insulator with a quite high  $T_N = 275$  K.<sup>27</sup> Upon Sr or Ca doping,  $\text{Co}^{3+}$  ions are introduced. Measurements of magnetic and transport properties of  $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$  ( $0.4 \leq x \leq 0.8$ ) led Moritomo *et al.* to a conclusion that the  $\text{Co}^{3+}$  ions undergo a spin state transition from HS ( $x \leq 0.6$ ) to IS ( $x \geq 0.8$ ).<sup>28</sup> Neutron scattering measurements of  $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$  by Zaliznyak *et al.* showed a checkerboard  $\text{Co}^{2+}$ - $\text{Co}^{3+}$  charge order and a strongly decreasing spin ordering temperature ( $T_{\text{SO}} \approx 30$  K), and they suggested the  $\text{Co}^{3+}$  ions to be in an IS but nonmagnetic state quenched by strong planar anisotropy.<sup>29,30</sup> The  $\text{Co}^{2+}$ - $\text{Co}^{3+}$  charge order was also observed in  $\text{La}_{1.5}\text{Ca}_{0.5}\text{CoO}_4$  and the  $\text{Co}^{3+}$  ions were suggested to be in a mixed IS+HS state.<sup>31,32</sup> In contrast, a magnetic susceptibility study of  $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$  ( $0.3 \leq x \leq 0.8$ ) and crystal-field model calculations indicated that the  $\text{Co}^{3+}$  must be in the LS state for  $x \geq 0.4$ .<sup>21</sup> In particular, a very recent x-ray absorption spectroscopic study by Chang *et al.* established a picture of HS  $\text{Co}^{2+}$  and LS  $\text{Co}^{3+}$  for  $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ , and their study well accounts for the extremely insulating nature of the  $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$  series, the high charge ordering temperature and low  $T_{\text{SO}}$  of  $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ .<sup>26</sup>

It is, however, a bit surprising that this interesting material and the spin state issue received much less theoretical investigation. Previous unrestricted Hartree-Fock calculations showed that there are two spin-state transitions in  $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$  in the doping range of  $0 < x < 1.1$ , and that  $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$  is in the ferromagnetic HS state.<sup>33</sup> In view of the existing controversy, the spin state of the charge ordered  $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$  remains to be an open question, and therefore we will shed light on this issue by carrying out a set of density functional electronic structure calculations. Our results show that  $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$  is indeed in the HS- $\text{Co}^{2+}$ /LS- $\text{Co}^{3+}$  ground state, which can explain the experiments as seen below. However, the energetically unfavorable IS or HS  $\text{Co}^{3+}$  state would have a trouble in such an explanation.

We used the structural data of  $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$  measured by single-crystal neutron diffraction.<sup>34</sup> Our electronic structure calculations were performed by using the full-potential augmented plane waves plus local orbital method.<sup>35</sup> The muffin-tin sphere radii are chosen to be 2.5, 2.0, and 1.5 Bohr for La/Sr, Co, and O atoms, respectively. A virtual atom with an atomic number  $Z = 56.75$  ( $0.75Z_{\text{La}} + 0.25Z_{\text{Ba}}$ ) is used for the  $(\text{La}_{1.5}\text{Sr}_{0.5})$  sites since La and Sr(Ba) ions are in most cases simply electron donors. The cutoff energy of 16 Ryd is used for plane-wave expansion, and 600 **k** points for integrations over the Brillouin zone. To account for the strong electron correlations, the local-spin-density approximation plus Hubbard  $U$  (LSDA+ $U$ ) (Ref. 36) calculations were carried out, with  $U = 5$  eV and Hund exchange of 0.9 eV for the Co 3d electrons.<sup>37,38</sup> The SOC turns out to be quite important and it is included by the second-variational method with scalar relativistic wave functions.<sup>35</sup>

Usually, LSDA+ $U$  calculations may yield different orbital-polarized solutions, depending on the initialized occupation number matrix. Talking about the spin state issue, we have done a set of LSDA+ $U$ +SOC calculations which are initialized by assuming the LS, IS, and HS states, respectively. Our results show that while the  $\text{Co}^{2+}$  ion in  $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$  is always stabilized at the normal HS state, the  $\text{Co}^{3+}$  can be stabilized at the LS, IS, or HS state, as detailed below. It is important to note that the total-energy results reveal the  $\text{Co}^{3+}$  LS ground state.

Figure 1 shows the density of states in the HS- $\text{Co}^{2+}$ /LS- $\text{Co}^{3+}$  ground state. The HS  $\text{Co}^{2+}$  has the  $t_{2g}^5 e_g^2$

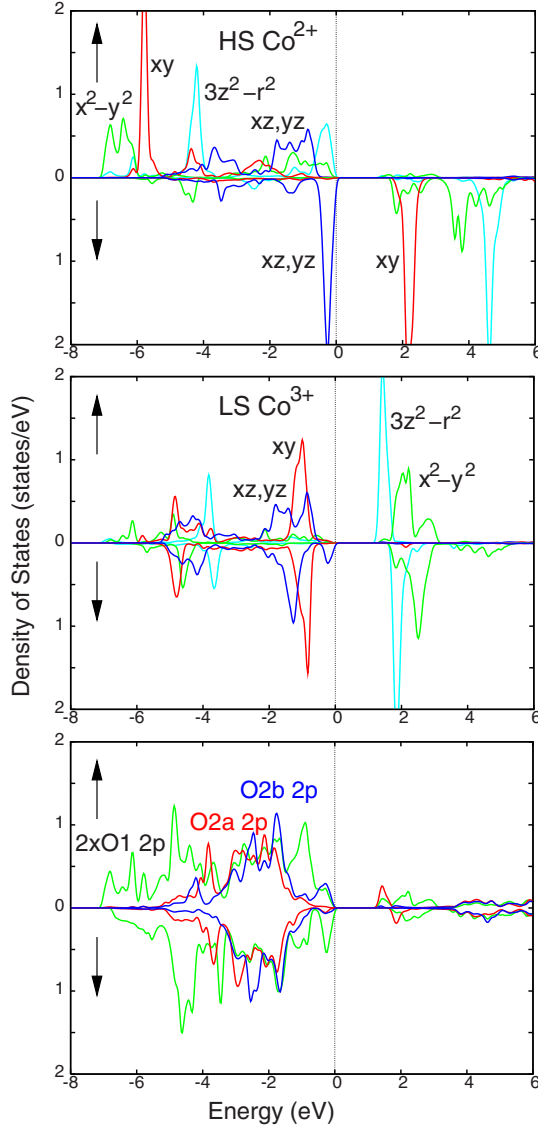


FIG. 1. (Color online) Density of states (DOS) of the HS-Co<sup>2+</sup>/LS-Co<sup>3+</sup> ground state of La<sub>1.5</sub>Sr<sub>0.5</sub>CoO<sub>4</sub> calculated by LSDA+*U*+SOC. The HS Co<sup>2+</sup> has  $t_{2g}^5 e_g^2$  with a  $t_{2g}$  hole on the  $xy$  orbital, and the LS Co<sup>3+</sup> closed  $t_{2g}^6$  shell. The 2*p* DOS of the planar O1, Co<sup>3+</sup>-apical O2a, and Co<sup>2+</sup>-apical O2b are also shown. Fermi level is set at zero energy.

configuration with one  $t_{2g}$  hole on the  $xy$  orbital. This corresponds to the local crystal field: since the out-of-plane Co<sup>2+</sup>-O2*b* bondlength of 2.192 Å is much bigger than the in-plane Co<sup>2+</sup>-O1 bondlength of 1.955 Å,<sup>34</sup> the  $xy$  level should be higher than the  $xz/yz$  and it is the  $t_{2g}$  hole orbital. The  $t_{2g}$  crystal field splitting (CFS) and especially electron correlations open a gap between the  $xz/yz$  and  $xy$  in the down-spin channel. For the LS Co<sup>3+</sup> ion, it has a closed  $t_{2g}^6$  shell which allows one to calculate the  $t_{2g}$  interior small CFS by simply determining the center of gravity of each orbital-resolved density of states. The calculated ionic CFS between the higher  $xy$  level and lower  $xz/yz$  is 70 meV. However, for the HS Co<sup>2+</sup> with an open  $t_{2g}$  shell, the LSDA self-interaction error of the lower-lying occupied orbital obscures an estimate of a small  $t_{2g}$  CFS (For the closed  $t_{2g}^6$  shell, however, the self-interaction errors are common for each  $t_{2g}$  orbital and thus counteracted). Instead, we used a  $\sqrt{2} \times \sqrt{2} \times 1$  supercell and replaced one Co<sup>2+</sup> by an immediate neighbor Ni<sup>2+</sup> ( $S=1$ ,  $t_{2g}^6 e_g^2$ ) which has a closed  $t_{2g}$  shell. Thus the Co<sup>2+</sup>  $t_{2g}$  CFS is estimated to be about 30 meV between the  $xy$  and  $xz/yz$ . Note that the smaller CFS of the Co<sup>2+</sup>  $t_{2g}$  levels than that of the Co<sup>3+</sup>  $t_{2g}$  is consistent with the larger Co-O bondlengths of the former.<sup>34</sup> Owing to the small CFS of the open  $t_{2g}$  shell at the Co<sup>2+</sup> site, the SOC is operative and mixes the lower-lying  $xz/yz$  with higher  $xy$  level and thus produces an in-plane orbital magnetic moment. Our LSDA+*U*+SOC calculations show that La<sub>1.5</sub>Sr<sub>0.5</sub>CoO<sub>4</sub> has an easy in-plane magnetism and an orbital moment of  $0.26\mu_B$  per Co<sup>2+</sup> (reduced by Co-O covalent effects), as well as an almost quenched orbital moment of  $0.02\mu_B$  at the LS Co<sup>3+</sup> site due to the closed  $t_{2g}$  shell, as seen in Table I. The solution with an easy out-of-plane magnetism was calculated to have a higher energy by 12 meV per Co<sup>2+</sup> and the corresponding Co<sup>2+</sup> orbital moment is only  $0.01\mu_B$ . Thus, our results, based on the HS-Co<sup>2+</sup>/LS-Co<sup>3+</sup> ground state solution, account for the experimentally observed easy in-plane magnetism of La<sub>1.5</sub>Sr<sub>0.5</sub>CoO<sub>4</sub>.<sup>21,28</sup> Moreover, this ground state displays a narrow band insulating behavior with a band gap of 1.2 eV (Fig. 1) which is in agreement with an optical conductivity measurement,<sup>39</sup> and the observed spectral peak around 3 eV can be explained as a charge transfer excitation from the in-plane O1 2*p* at about -1 eV to the Co<sup>2+</sup>  $xy$  and Co<sup>3+</sup>  $x^2-y^2$  both at 2 eV.

TABLE I. Total energies (in unit of meV per 2 f.u.) of La<sub>1.5</sub>Sr<sub>0.5</sub>CoO<sub>4</sub> having the LS, IS, or HS Co<sup>3+</sup> state and a robust HS Co<sup>2+</sup> calculated by LSDA+*U*+SOC. The HS Co<sup>2+</sup> configuration is shown only once in the LS-Co<sup>3+</sup>/HS-Co<sup>2+</sup> ground state. Except for the ground state having an easy in-plane magnetism (the spin and orbital moments in unit of  $\mu_B$  marked by a subscript “*ab*”), all other solutions have a wrong easy out-of-plane magnetism.

State and configuration	Energy	Co <sup>3+</sup> <sub>spin</sub>	Co <sup>3+</sup> <sub>orb</sub>	Co <sup>2+</sup> <sub>spin</sub>	Co <sup>2+</sup> <sub>orb</sub>	Figure
LS Co <sup>3+</sup> ( $t_{2g}^6$ )/HS Co <sup>2+</sup> ( $t_{2g}^3 e_g^2$ , $xz_{\uparrow}^1 yz_{\downarrow}^1$ )	0	0.29 <sub>ab</sub>	0.02 <sub>ab</sub>	2.52 <sub>ab</sub>	0.26 <sub>ab</sub>	Figure 1
LS Co <sup>3+</sup> ( $t_{2g}^6$ )/HS Co <sup>2+</sup>	12	0.29	0.05	2.52	0.01	
IS Co <sup>3+</sup> [ $t_{2g}^3 (3z^2-r^2)_{\uparrow}^1 xz_{\uparrow}^1 yz_{\downarrow}^1$ ]/HS Co <sup>2+</sup>	725	-1.50	0	2.48	0.02	Figure 2(a)
IS Co <sup>3+</sup> [ $t_{2g}^3 (3z^2-r^2)_{\uparrow}^1 xy_{\uparrow}^1 (xz-iyz)_{\downarrow}^1$ ]/HS Co <sup>2+</sup>	298	-1.52	-1.08	2.51	0	Figure 2(b)
IS Co <sup>3+</sup> [ $t_{2g}^3 (3z^2-r^2)_{\uparrow}^1 xy_{\uparrow}^1 (xz+iyz)_{\downarrow}^1$ ]/HS Co <sup>2+</sup>	122	2.02	1.30	2.48	0.03	Figure 2(c)
HS Co <sup>3+</sup> [ $t_{2g}^2 e_g^2 (xz-iyz)_{\uparrow}^1$ ]/HS Co <sup>2+</sup>	311	-2.95	-0.96	2.45	0.02	

Since the  $\text{Co}^{2+}$  ion is always stabilized at the HS state as described above, in the following the spin state and electronic structure of the  $\text{Co}^{3+}$  ion only are further discussed. From the middle panel of Fig. 1, it can be seen that the  $3z^2 - r^2$  level is lower than the  $x^2 - y^2$  by 0.7 eV, in good agreement with an x-ray absorption spectroscopic study.<sup>26</sup> When a  $\text{Co}^{3+}$  IS state is realized, most probably one  $t_{2g}$  electron will be promoted to the  $3z^2 - r^2$  level rather than the much higher  $x^2 - y^2$ . Simply according to the crystal field level diagram, it is the  $xy$  electron which will be promoted to the  $3z^2 - r^2$ , as seen in Fig. 2(a). It is, however, important to note that the IS state has a significant multiplet effect. Because the  $3z^2 - r^2$  electron density has a bigger overlap and thus a stronger Coulomb repulsion with  $xz$  and  $yz$  than with  $xy$ ,<sup>21</sup> Coulomb interaction will strongly favor a promotion of one  $xz/yz$  electron, instead of the naively expected  $xy$  electron, to the  $3z^2 - r^2$  level. Indeed, this solution [see Fig. 2(b) and Table I] turns out to have a much lower total energy than the former [Fig. 2(a)] by about 430 meV per  $\text{Co}^{3+}$ , through our LSDA +  $U$  + SOC calculations for the antiferromagnetically coupled IS- $\text{Co}^{3+}$ /HS- $\text{Co}^{2+}$  states. Such a significant multiplet effect, which has been often omitted in *ab initio* electronic structure calculations, should be taken good care of when studying the intriguing spin state issue of cobaltates.<sup>8</sup>

As seen in Table I, the  $\text{Co}^{3+}$  IS state with one  $xz/yz$  hole lies higher in energy than the LS ground state by 298 meV and has a large out-of-plane orbital moment of  $-1.08\mu_B$  (parallel to the spin moment of  $-1.52\mu_B$ ) which consists of  $-0.8\mu_B$  from the complex orbital  $xz - iyz$  (namely,  $Y_{2-1}$  or  $d_{-1}$ ) and  $-0.28\mu_B$  from the  $xy + i(x^2 - y^2)$  ( $Y_{2-2}$  or  $d_{-2}$ ) due to the Coulomb interaction adjusted electron occupation.<sup>40</sup> Moreover, the IS  $\text{Co}^{3+}$  ion having an empty  $x^2 - y^2$  orbital and HS  $\text{Co}^{2+}$  having a singly occupied  $x^2 - y^2$  are expected to be ferromagnetically coupled in the *ab* basal plane, according to Goodenough-Kanamori-Anderson superexchange rules. This is supported by our result that the ferromagnetic IS- $\text{Co}^{3+}$ /HS- $\text{Co}^{2+}$  state is lower than the antiferromagnetic state by 176 meV (Table I), giving a strong in-plane ferromagnetism which is however in disagreement with the observed low  $T_{\text{SO}} \approx 30$  K. Furthermore, this lowest-lying  $\text{Co}^{3+}$  IS state [Fig. 2(c)] out of its multiplet is still higher than the LS ground state by 122 meV, and it has again a huge out-of-plane orbital moment of  $1.3\mu_B$  [ $0.8\mu_B$  from  $xz + iyz$  ( $Y_{21}$  or  $d_1$ ) and  $0.5\mu_B$  from  $xy - i(x^2 - y^2)$  ( $Y_{22}$  or  $d_2$ )], in contradiction with the observed easy in-plane magnetism. This supports an analysis of magnetic anisotropy by Hollmann *et al.*<sup>21</sup>

It might be a bit surprising that the  $\text{Co}^{3+}$  ion in  $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$  with a large distortion of the  $\text{CoO}_6$  octahedron does not have the IS as its ground state. We note that the large difference of the  $\text{Co}^{3+}$ -O bondlengths,  $1.888 \text{ \AA} \times 4$  vs  $2.077 \text{ \AA} \times 2$ ,<sup>34</sup> does not signal a strong Jahn-Teller (JT) distortion which may stabilize the IS state with a half-filled  $e_g$  orbital, since in the isostructural  $\text{La}_2\text{NiO}_4$  the non-JT ion  $\text{Ni}^{2+}$  has also very different bondlengths,  $1.95 \text{ \AA} \times 4$  vs  $2.22 \text{ \AA} \times 2$ .<sup>41</sup> The out-of-plane elongation of the  $\text{CoO}_6$  and  $\text{NiO}_6$  octahedra may well be a consequence of the reduction of internal strains in the single-layered perovskites. Although the large distortion of the  $\text{CoO}_6$  octahedron yields a pronounced  $e_g$  splitting of 0.7 eV as discussed above, it is far less than the required huge  $e_g$  splitting of about 2 eV via a JT

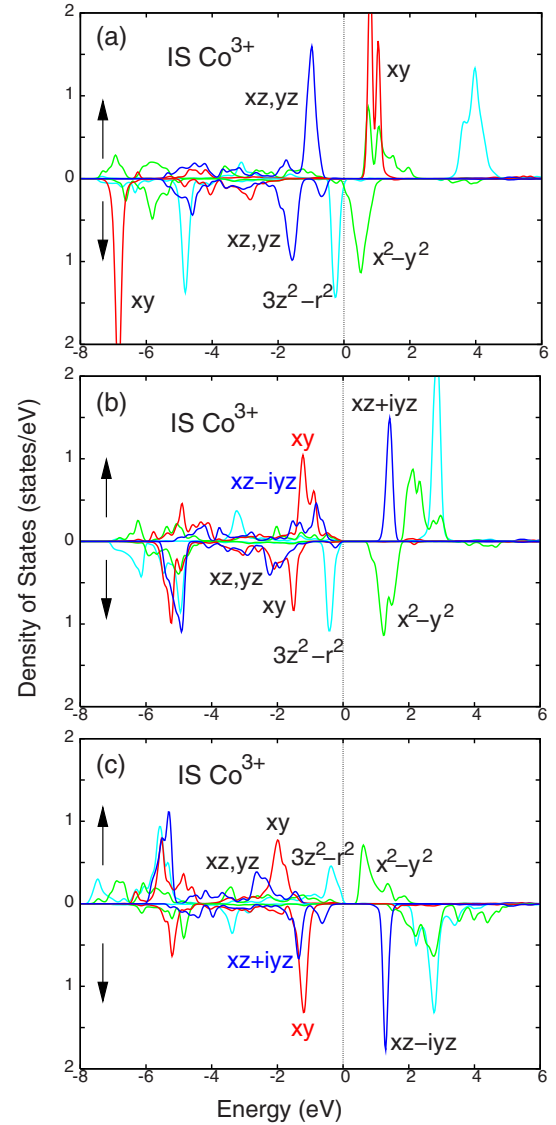


FIG. 2. (Color online) Density of states of the IS  $\text{Co}^{3+}$  ion in different configurations: (a)  $t_{2g}^3(3z^2 - r^2)^1xz^1yz^1$ , (b)  $t_{2g}^3(3z^2 - r^2)^1xy^1(xz - iyz)^1$ , and (c)  $t_{2g}^3(3z^2 - r^2)^1xy^1(xz + iyz)^1$ . The corresponding multiplet splitting is calculated to be several tenths of eV (see Table I). Note that the most favorable IS  $\text{Co}^{3+}$  state [configuration (c)], being ferromagnetically coupled with the robust HS  $\text{Co}^{2+}$  (not shown here but refer to Fig. 1), is still higher in energy than the LS  $\text{Co}^{3+}$  ground state by 122 meV and has a wrong easy out-of-plane magnetism (see Table I and main text).

distortion to stabilize the IS state as ground state.<sup>40</sup> In this sense, a stabilization of the IS state via the JT effect may need an astonishingly large distortion which seems however hardly to reach in real materials.

Now we turn to a possible  $\text{Co}^{3+}$  HS state. We first note that the HS  $\text{Co}^{3+}$  would have a strong antiferromagnetic coupling with the HS  $\text{Co}^{2+}$  as in the parent compound  $\text{La}_2\text{CoO}_4$  with a quite high  $T_N$  of 275 K, in contrast to the low  $T_{\text{SO}} \approx 30$  K of  $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ . This already infers that a HS  $\text{Co}^{3+}$  state is quite unlikely. Indeed, our calculations show that the HS  $\text{Co}^{3+}$  state is higher in energy than the LS ground state by 311 meV and that it has a big out-of-plane orbital



moment of  $-0.96\mu_B$  (parallel to its spin moment of  $-2.95\mu_B$ , see Table I) being again in disagreement with the observed easy in-plane magnetism.

To conclude, we confirm that the checkerboard charge order in  $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$  consists of the HS  $\text{Co}^{2+}$  and LS  $\text{Co}^{3+}$ , through a set of LSDA+ $U$  band structure calculations including the spin-orbit coupling and multiplet effect. This solution accounts for the optical spectra. The small  $\text{Co}^{2+}$   $t_{2g}$  crystal field splitting makes the spin-orbit coupling operative, which produces the observed easy in-plane magnetism.

In contrast, either the higher-lying IS or highest HS  $\text{Co}^{3+}$  states would yield a wrong easy out-of-plane magnetism. Moreover, the IS (HS)  $\text{Co}^{3+}$  would have strong ferromagnetic (antiferromagnetic) coupling with the robust HS  $\text{Co}^{2+}$ , both in disagreement with the low spin-ordering temperature of  $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ . Finally we note that the multiplet effect of the IS state is significant and should be taken good care of.

This work was supported by the Deutsche Forschungsgemeinschaft through SFB 608.

- <sup>1</sup>K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R. A. Dilanian, and T. Sasaki, *Nature (London)* **422**, 53 (2003).
- <sup>2</sup>I. O. Troyanchuk, N. V. Kasper, D. D. Khalyavin, H. Szymczak, R. Szymczak, and M. Baran, *Phys. Rev. Lett.* **80**, 3380 (1998).
- <sup>3</sup>I. Terasaki, Y. Sasago, and K. Uchinokura, *Phys. Rev. B* **56**, R12685 (1997).
- <sup>4</sup>J. B. Goodenough, *J. Phys. Chem. Solids* **6**, 287 (1958).
- <sup>5</sup>M. Zhuang, W. Zhang, and N. Ming, *Phys. Rev. B* **57**, 10705 (1998).
- <sup>6</sup>S. Noguchi, S. Kawamata, K. Okuda, H. Nojiri, and M. Motokawa, *Phys. Rev. B* **66**, 094404 (2002).
- <sup>7</sup>Z. Ropka and R. J. Radwanski, *Phys. Rev. B* **67**, 172401 (2003).
- <sup>8</sup>M. W. Haverkort, Z. Hu, J. C. Cezar, T. Burnus, H. Hartmann, M. Reuther, C. Zobel, T. Lorenz, A. Tanaka, N. B. Brookes, H. H. Hsieh, H.-J. Lin, C. T. Chen, and L. H. Tjeng, *Phys. Rev. Lett.* **97**, 176405 (2006).
- <sup>9</sup>A. Podlesnyak, S. Streule, J. Mesot, M. Medarde, E. Pomjakushina, K. Conder, A. Tanaka, M. W. Haverkort, and D. I. Khomskii, *Phys. Rev. Lett.* **97**, 247208 (2006).
- <sup>10</sup>M. A. Korotin, S. Yu. Ezhov, I. V. Solov'yev, V. I. Anisimov, D. I. Khomskii, and G. A. Sawatzky, *Phys. Rev. B* **54**, 5309 (1996).
- <sup>11</sup>R. F. Klie, J. C. Zheng, Y. Zhu, M. Varela, J. Wu, and C. Leighton, *Phys. Rev. Lett.* **99**, 047203 (2007).
- <sup>12</sup>S. K. Pandey, A. Kumar, S. Patil, V. R. R. Medicherla, R. S. Singh, K. Maiti, D. Prabhakaran, A. T. Boothroyd, and A. V. Pimpale, *Phys. Rev. B* **77**, 045123 (2008).
- <sup>13</sup>J. M. Rondinelli and N. A. Spaldin, *Phys. Rev. B* **79**, 054409 (2009).
- <sup>14</sup>T. Kyômen, Y. Asaka, and M. Itoh, *Phys. Rev. B* **71**, 024418 (2005).
- <sup>15</sup>K. Knížek, Z. Jiráček, J. Hejtmánek, P. Herry, and G. André, *J. Appl. Phys.* **103**, 07B703 (2008).
- <sup>16</sup>M. Tachibana, T. Yoshida, H. Kawaji, T. Atake, and E. Takayama-Muromachi, *Phys. Rev. B* **77**, 094402 (2008).
- <sup>17</sup>K. Knížek, Z. Jiráček, J. Hejtmánek, P. Novák, and Wei Ku, *Phys. Rev. B* **79**, 014430 (2009).
- <sup>18</sup>Y. Shimada, S. Miyasaka, R. Kumai, and Y. Tokura, *Phys. Rev. B* **73**, 134424 (2006).
- <sup>19</sup>A. V. Chichev, M. Dlouhá, S. Vratilav, K. Knížek, J. Hejtmánek, M. Maryško, M. Veverka, Z. Jiráček, N. O. Golosova, D. P. Kozlenko, and B. N. Savenko, *Phys. Rev. B* **74**, 134414 (2006).
- <sup>20</sup>A. T. Savici, I. A. Zaliznyak, G. D. Gu, and R. Erwin, *Phys. Rev. B* **75**, 184443 (2007).
- <sup>21</sup>N. Hollmann, M. W. Haverkort, M. Cwik, M. Benomar, M. Reuther, A. Tanaka, and T. Lorenz, *New J. Phys.* **10**, 023018 (2008).
- <sup>22</sup>R. Ang, Y. P. Sun, X. Luo, C. Y. Hao, and W. H. Song, *J. Phys. D: Appl. Phys.* **41**, 045404 (2008).
- <sup>23</sup>K. Horigane, T. Kobayashi, M. Suzuki, K. Abe, K. Asai, and J. Akimitsu, *Phys. Rev. B* **78**, 144108 (2008).
- <sup>24</sup>N. Sakiyama, I. A. Zaliznyak, S.-H. Lee, Y. Mitsui, and H. Yoshizawa, *Phys. Rev. B* **78**, 180406(R) (2008).
- <sup>25</sup>M. Cwik, M. Benomar, T. Finger, Y. Sidis, D. Senff, M. Reuther, T. Lorenz, and M. Braden, *Phys. Rev. Lett.* **102**, 057201 (2009).
- <sup>26</sup>C. F. Chang, Z. Hu, H. Wu, T. Burnus, N. Hollmann, M. Benomar, T. Lorenz, A. Tanaka, H.-J. Lin, H. H. Hsieh, C. T. Chen, and L. H. Tjeng, *Phys. Rev. Lett.* **102**, 116401 (2009).
- <sup>27</sup>K. Yamada, M. Matsuda, Y. Endoh, B. Keimer, R. J. Birgeneau, S. Onodera, J. Mizusaki, T. Matsuura, and G. Shirane, *Phys. Rev. B* **39**, 2336 (1989).
- <sup>28</sup>Y. Moritomo, K. Higashi, K. Matsuda, and A. Nakamura, *Phys. Rev. B* **55**, R14725 (1997).
- <sup>29</sup>I. A. Zaliznyak, J. P. Hill, J. M. Tranquada, R. Erwin, and Y. Moritomo, *Phys. Rev. Lett.* **85**, 4353 (2000).
- <sup>30</sup>I. A. Zaliznyak, J. M. Tranquada, R. Erwin, and Y. Moritomo, *Phys. Rev. B* **64**, 195117 (2001).
- <sup>31</sup>K. Horigane, H. Hiraka, T. Uchida, K. Yamada, and J. Akimitsu, *J. Phys. Soc. Jpn.* **76**, 114715 (2007).
- <sup>32</sup>K. Horigane, H. Nakao, Y. Kousaka, T. Murata, Y. Noda, Y. Murakami, and J. Akimitsu, *J. Phys. Soc. Jpn.* **77**, 044601 (2008).
- <sup>33</sup>J. Wang, Y. C. Tao, Weiyi Zhang, and D. Y. Xing, *J. Phys.: Condens. Matter* **12**, 7425 (2000).
- <sup>34</sup>M. Cwik, Ph.D. thesis, Universität zu Köln, 2007. The charge ordered structure data: space group *Bmmm* (No. 65); lattice constant  $a=b=5.435 \text{ \AA}$  and  $c=12.560 \text{ \AA}$ ; atomic positions  $\text{La1/Sr1 } 4i$  (0, 0, 0.3611),  $\text{La2/Sr2 } 4j$  (0.5, 0, 0.1379),  $\text{Co}^{3+} 2a$  (0, 0, 0),  $\text{Co}^{2+} 2c$  (0.5, 0.5, 0),  $\text{O1 } 8o$  (0.2463, 0.2450, 0),  $\text{O2a } 4i$  (0, 0, 0.1654), and  $\text{O2b } 4j$  (0.5, 0.5, 0.1745); bondlengths  $\text{Co}^{3+}\text{-O1}=1.888 \text{ \AA} \times 4$ ,  $\text{Co}^{3+}\text{-O2a}=2.077 \text{ \AA} \times 2$ ,  $\text{Co}^{2+}\text{-O1}=1.955 \text{ \AA} \times 4$ ,  $\text{Co}^{2+}\text{-O2b}=2.192 \text{ \AA} \times 2$ .
- <sup>35</sup>P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, WIEN2K package, <http://www.wien2k.at>
- <sup>36</sup>V. I. Anisimov, I. V. Solov'yev, M. A. Korotin, M. T. Czyzyk, and G. A. Sawatzky, *Phys. Rev. B* **48**, 16929 (1993).
- <sup>37</sup>W. E. Pickett, S. C. Erwin, and E. C. Ethridge, *Phys. Rev. B* **58**, 1201 (1998).
- <sup>38</sup>H. Wu, M. W. Haverkort, Z. Hu, D. I. Khomskii, and L. H. Tjeng, *Phys. Rev. Lett.* **95**, 186401 (2005).
- <sup>39</sup>S. Uchida, H. Eisaki, and S. Tajima, *Physica B* **186-188**, 975 (1993).
- <sup>40</sup>M. W. Haverkort, Ph.D. thesis, Universität zu Köln, 2005.
- <sup>41</sup>G. H. Lander, P. J. Brown, J. Spalek, and J. M. Honig, *Phys. Rev. B* **40**, 4463 (1989).